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Harandi et al.

[11] **Patent Number: 5,001,292**
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[54] **ETHER AND HYDROCARBON PRODUCTION**

[75] Inventors: **Mohsen N. Harandi**, Lawrenceville; **Hartley Owen**, Belle Mead, both of N.J.

[73] Assignee: **Mobil Oil Corporation**, New York, N.Y.

[*] Notice: The portion of the term of this patent subsequent to May 30, 2006 has been disclaimed.

[21] Appl. No.: **422,203**

[22] Filed: **Oct. 16, 1989**

Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 349,555, May 9, 1989, which is a division of Ser. No. 130,260, Dec. 8, 1987, Pat. No. 4,854,939.

[51] **Int. Cl.**^{5} **C07C 1/20;** C07C 2/00

[52] **U.S. Cl.** **585/322;** 585/310; 585/314; 585/408; 585/469; 585/640; 568/697; 568/698; 44/449

[58] **Field of Search** 568/697, 698, 699; 585/640, 322, 310, 324, 314, 408, 469; 44/77

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,760,024	9/1973	Cattanach	585/418
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4,826,507	5/1989	Harandi et al.	568/697
4,830,635	5/1989	Harandi et al.	44/56
4,835,329	5/1989	Harandi et al.	585/407
4,854,939	8/1989	Harandi et al.	585/415
4,857,664	8/1989	Huang et al.	568/695

Primary Examiner—Anthony McFarlane
Attorney, Agent, or Firm—Alexander J. McKillop; Charles J. Speciale; L. G. Wise

[57] **ABSTRACT**

An integrated process is disclosed that substantially reduces the cost of producing MTBE and other alkyl tert-alkyl ethers by eliminating a major portion of the equipment and operating costs associated with the downstream processing of the etherification reactor effluent. The integrated process combines the process for the etherification of isoolefins and methanol, or other alkanols, to produce methyl tertiary alkyl ethers such as MTBE and/or TAME with the catalytic process for converting feedstock such as oxygenates, light olefins and paraffins to higher molecular weight hydrocarbons. Unconverted reactants from the etherification reaction, which may comprise unreacted alkanol and unreacted hydrocarbons or just unreacted hydrocarbons, are separated from the product ethers and passed to the catalytic conversion process reactor for conversion to gasoline boiling range hydrocarbons.

27 Claims, 1 Drawing Sheet

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ETHER AND HYDROCARBON PRODUCTION

REFERENCE TO COPENDING APPLICATIONS

This application is a continuation-in-part of U.S. patent application Ser. No. 349,555 filed May 9, 1989 now pending which is a division of U.S. patent application Ser. No. 130,260 filed Dec. 8, 1987 now U.S. Pat. No. 4,854,939.

BACKGROUND OF THE INVENTION

This invention relates to methods for reacting aliphatic alcohol (alkanol), such as methanol or the like and olefinic hydrocarbons to produce lower alkyl tertiary-alkyl ethers without the need for recycling unreacted alkanol and/or hydrocarbon. In particular, this invention relates to a continuous integrated system for converting methanol to high octane ether and gasoline by etherifying hydrocarbons containing iso-olefins, such as the C_3–C_4 olefinic cracked gas streams obtained from fluid catalytic cracking (FCC) products.

It is known that isobutylene and other isoalkenes produced by hydrocarbon cracking may be reacted with methanol and other C1–C4 lower aliphatic alcohols over an acidic catalyst to provide methyl tertiary butyl ether (MTBE) or the like. Generally, it is known that asymmetrical ethers having the formula $(CH_3)_3C—O—R$, where R is a C1–C4 alkyl radical, are particularly useful as octane improvers for liquid fuels, especially gasoline.

MTBE, ethyl t-butyl ether (ETBE), tert-amyl methyl ether (TAME) and isopropyl t-butyl ether (IPTBE) are known to be high octane ethers. The article by J. D. Chase, et al., *Oil and Gas Journal*, Apr. 9, 1979, discusses the advantages one can achieve by using such materials to enhance gasoline octane. The octane blending number of MTBE when 10% is added to a base fuel ($R+O=91$) is about 120. For a fuel with a low motor rating ($M+O=83$) octane, the blending value of MTBE at the 10% level is about 103. On the other hand, for an ($R+O$) of 95 octane fuel, the blending value of 10% MTBE is about 114.

While it is known that isobutylene and/or isoamylene may be reacted with methanol over an acidic catalyst to provide MTBE and/or TAME, a problem of major importance in these processes is the separation of unreacted methanol and hydrocarbons from the etherification reaction product due to the proclivity of methanol to form a very dilute azeotropic mixture with hydrocarbons and the strong solubility of methanol in both water and hydrocarbons. But, to achieve high iso-olefin conversion to ethers equimolar or larger quantities of methanol are preferred in the etherification reaction, producing unreacted methanol. Due largely to these factors, the cost associated with methanol separation and recycling in the etherification reaction represents a large part of the cost of the total etherification process.

In recent years, a major development within the petroleum industry has been the discovery of the special catalytic capabilities of a family of zeolite catalyst based upon medium pore size shape selective metallosilicates. Discoveries have been made leading to a series of analogous processes drawn from the catalytic capability of zeolites. Depending upon various conditions of space velocity, temperature and pressure lower oxygenates, such as methanol can be converted in the presence of zeolite type catalyst to olefins which can oligomerize to provide gasoline or distillate or can be converted further to produce aromatics. Recognizing the commonality of the feedstock and product between etherification reactions to produce high octane gasoline and zeolite catalyzed conversion reactions, interest has focused on the applicability of combined processes as an approach to advance the art in the production of high octane gasoline.

It has been discovered that under certain conditions substantial improvements in the art of alkyl tert-alkyl ether production can be realized in a combination or integration of etherification and hydrocarbon conversion processes based upon zeolite type catalysis. Accordingly, it is an object of this invention to provide a novel integrated process for the production alkyl tert-alkyl ethers, particularly MTBE and/or TAME.

Another object of this invention is to provide a novel and cost effective process for the production of high octane alkyl tertiary alkyl ethers without recycling unreacted alkanol and/or unreacted hydrocarbons to the etherification reactor.

Yet another object of the present invention is to provide a novel process for the production of high octane gasoline rich in aromatics utilizing unreacted methanol from etherification.

SUMMARY OF THE INVENTION

An integrated process has been discovered that substantially reduces the cost of producing ether by eliminating a major portion of the equipment and operating costs associated with the downstream processing of the etherification reactor effluent. The integrated process combines the process for the etherification of iso-olefins and methanol, or other alkanols, to produce methyl tertiary alkyl ethers such as MTBE and/or TAME with the catalytic process for converting feedstock such as oxygenates, light olefins and paraffins to higher molecular weight hydrocarbons. Unconverted reactants from the etherification reaction, which may comprise unreacted alkanol and/or unreacted hydrocarbons, are separated from the product ethers and passed to the catalytic reactor for conversion to gasoline boiling range hydrocarbons.

More particularly, a continuous process for converting alkanol to alkyl tertiary-alkyl ethers and gasoline boiling range hydrocarbons has been discovered which comprises the steps of:

(a) contacting alkanol and a light olefinic hydrocarbon stream rich in isobutylene and other C_4 isomeric hydrocarbons under iso-olefins etherification conditions in an etherification reaction zone containing acid etherification catalyst;

(b) separating the etherification effluent from step (a) to recover an upper stream comprising unreacted alkanol and light olefinic hydrocarbon and a liquid stream containing alkyl tertiary-butyl ether; and

(c) contacting said unreacted alkanol and light hydrocarbon stream with acidic catalyst, preferably medium pore metallosilicate catalyst, under alkanol and hydrocarbon conversion conditions whereby gasoline boiling range hydrocarbons are produced.

DESCRIPTION OF THE DRAWING

FIG. 1 of the drawing is a schematic etherification process flowsheet depicting the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Typical feedstock materials for etherification reactions include olefinic streams, such as FCC light cracked gas containing butene isomers, often in mixture with substantial amounts of propene, propane, n-butane and isobutane. The C_4 components usually contain a major amount of unsaturated compounds, such as 10–25% isobutylene, 25–55% linear butenes, and small amounts of butadiene. Also, C_4+ heavier olefinic hydrocarbon streams may be used, particularly mixtures of isobutylene and isoamylene. These aliphatic streams are produced in a variety of petroleum refinery operation such as catalytic cracking of gas oil or the like. The dry methanol feedstream should preferably have a purity of about 99.8 wt %.

Suitable alkanols include C_1–C_4 primary or secondary alcohols, including methanol, ethanol, 1-propanol, isopropanol, 1-butanol, 2-butanol and mixtures thereof.

Referring to FIG. 1 of the drawing, a continuous stream of C_4-olefinic hydrocarbon liquid is introduced via conduit **12** to pre-separation unit **14** and guard bed **15** and mixed with dry methanol (MeOH) feedstock introduced via conduit **10**. The combined streams are pressurized to about 1190 kPa (170 psig), heated in exchanger **16** to a temperature of about 55° C. (130° F.) and passed to a first serial reactor **20** for conversion of methanol in contact with acid etherification catalyst, preferably solid polysulfonic acid resin such as sulfonated vinyl aromatic resins. Amberlyst **15** from Rohm and Haas is a preferred catalyst. From first reactor **20** the reaction stream is cooled in exchanger **22** from about 70° C. to 55° C. and further reacted in a second serial reactor **24**, where the reaction is carried partially to completion (e.g., 96% conversion of isobutylene).

The reactor effluent stream containing MTBE, methanol and unreacted light hydrocarbons is preheated in exchanger **26** and fed to debutanizer fractionation tower **30**. In separation unit **30** the C5+ methyl tert-alkyl ether product is recovered as a liquid product, along with byproduct dimer or other heavier hydrocarbons in the effluent. Tower overhead vapor comprising unreacted C_4- light hydrocarbons and methanol are passed via conduit **32** and heat exchange means **34**, **36** to an effluent upgrading reactor **40**. The catalytic conversion unit **40** is preferably a fluid bed unit, equipped with a catalyst regenerator **42**. Reactor effluent may be fractionated in a debutanizer tower **45** to recover a gasoline product stream **46**, C_3–C_4 LPG stream **47**, and off-gas **48**.

The methanol-containing stream, preferably a vapor stream, may be coreacted with olefinic light gas and/or other reactive hydrocarbon feedstreams in an oligomerization/aromatization reaction section, as described by Avidan et al. in U.S. Pat. Nos. 4,547,616 and 4,746,762 and by Owen et al. in U.S. Pat. Nos. 4,827,046 and 4,831,203, incorporated herein by reference. Optionally, FCC light gas containing ethene or propene may be injected at the bottom of the fluidized bed reaction zone and converted along with the unreacted methanol containing fractions of the light hydrocarbon etherification effluent stream.

The following Example provides a detailed illustration of the process of this invention for a refinery operation processing methanol and C_4 feedstock to produce MTBE and hydrocarbon conversion products containing about 22 mole percent of gasoline products. The gasoline products are about 55 weight percent aromatics, 15 weight percent olefins, with the balance paraffins.

EXAMPLE

About 530.36 moles/hr of feedstock is passed to the etherification reactor system as described in FIG. 1. The feedstock contains 69 moles/hr of methanol and hydrocarbons consisting of 12 moles/hr of C_3's, 129.45 moles/hr of isobutane, 219.18 moles/hr of 1-butene, 25.09 moles/hr of n-butane and 71.18 moles/hr of isobutene and 4.46 moles/hr of C_5+ hydrocarbons. Following etherification, the effluent therefrom contains 66.87 moles/hr of MTBE, 2.09 moles/hr of unreacted methanol, 4.27 moles/hr of unreacted isobutene, 12 moles/hr of C_3's, 129.45 moles/hr of isobutane, 219.18 moles/hr of 1-butene, 25.09 moles/hr of n-butane and 4.46 moles/hr of C_5+. MTBE is recovered following debutanization and debutanized overhead vapor is passed to the fluidized bed zeolite conversion zone for contact with ZSM-5 catalyst under conversion conditions previously described in reference to FIG. 1. The conversion is carried out at a temperature of 480° C. (900° F.) and 925 kPa (135 psia) to produce 354.16 moles/hr of effluent. The product stream consists essentially of water (2.09 moles/hr), C_5+ gasoline (77.87 moles/hr), isobutene (6.63 moles/hr), n-butane (39.21 moles/hr), 1-butene (6.63 moles/hr), isobutane (153.71 moles/hr), propane (37.98 moles/hr), propene (14.32 moles/hr), ethane (3.84 moles/hr), ethene (8.68 moles/hr), and methane (3.20 moles/hr).

Etherification Operation

The reaction of methanol with isobutylene and isoamylenes at moderate conditions with a resin catalyst is known technology, as provided by R. W. Reynolds, et al., *The Oil and Gas Journal*, June 16, 1975, and S. Pecci and T. Floris, *Hydrocarbon Processing*, Dec. 1977. An article entitled "MTBE and TAME—A Good Octane Boosting Combo," by J. D. Chase, et al., *The Oil and Gas Journal*, Apr. 9, 1979, pages 149–152, discusses the technology. A preferred catalyst is a polymeric sulfonic acid exchange resin such as Amberlyst 15.

In the etherification process it is known that alkanol and iso-olefins may be reacted in equimolar quantities or either reactant may be in molar excess to influence the complete conversion of the other reactant. Because etherification is an incomplete reaction the etherification effluent comprises unreacted alkanol and unreacted hydrocarbons. On a stoichiometric equivalencies basis, equimolar quantities of methanol and iso-olefins are advantageous but an excess between 2 and 200% of either component can be passed to the etherification reaction unit. In the present invention, the molar ratio of alkanol to iso-olefin, such as methanol to iso-butylene, can be between 0.7 and 2, but preferably the molar ratio is 1 for methanol to isobutylene. Advantageously, the excess methanol may be about 40% or more when the hydrocarbon feedstream comprises significant quantity of isoamylenes, but equimolar quantities are preferred when the hydrocarbon feedstream consists essentially of C_4 hydrocarbons.

Iso-olefins or isoalkenes in this invention are those having the formula $R_2C{=}CH_2$ or $R_2C{=}CHR$. Alkanols which may be used in the present invention include methanol, ethanol, 1-propanol, isopropanol, 1-butanol and 2-butanol. In this invention oxygenate or lower oxygenates refers to C_1–C_5 alcohols, ethers, aldehydes, esters and the like.

METHANOL AND/OR HYDROCARBONS CONVERSION

It is advantageous to convert substantially the entire stream of unreacted alcohol and light olefinic components recovered from etherification effluent by acid zeolite catalysis, thus providing a once-through process without expensive alcohol recycle to the etherification unit. Zeolite conversion technology for upgrading lower aliphatic hydrocarbons and oxygenates to liquid hydrocarbon products, including gasoline boiling range hydrocarbons and aromatics, are well known. Commercial Methanol-to-Gasoline (MTG), methanol-to olefins (MTO), Mobil Olefin to Gasoline/Distillate (MOG/D) and conversion of olefins and paraffins to aromatics (M-2 Forming) processes employ shape selective medium pore zeolite catalysts. It is understood that the present zeolite conversion unit operation can have the characteristics of these catalysts and processes to produce a variety of hydrocarbon products, especially liquid aliphatics and aromatics in the C5–C9 gasoline range. The zeolite catalyzed conversion processes can be run in fixed, fluidized or moving catalyst beds.

The various reactions which take place in the zeolite conversion reactor include oligomerization, alkylation, dehydrocyclization, isomerization and cracking. These include exothermic and endothermic reactions, which can be thermally balanced to require little or no heat exchange to maintain process reaction temperature in the fluidized bed. Mixed hydrocarbons from FCC operations, following the etherification and effluent separation, can be selected or modified to include a balance of olefins and paraffins to achieve the desired thermodynamic properties.

Description of Zeolite Catalysts

Recent developments in zeolite technology have provided a group of medium pore siliceous materials having similar pore geometry. Most prominent among these intermediate pore size zeolites is ZSM-5, which is usually synthesized with Bronsted acid active sites by incorporating a tetrahedrally coordinated metal, such as Al, Ga, Fe or mixtures thereof, within the zeolitic framework. These medium pore zeolites are favored for acid catalysis; however, the advantages of ZSM-5 structures may be utilized by employing highly siliceous materials or crystalline metallosilicate having one or more tetrahedral species having varying degrees of acidity. ZSM-5 crystalline structure is readily recognized by its X-ray diffraction pattern, which is described in U.S. Pat. No. 3,702,866 (Argauer, et al.), incorporated by reference.

Zeolite hydrocarbon upgrading catalysts preferred for use herein include the medium pore (i.e., about 5–7A) shape-selective crystalline aluminosilicate zeolites having a silica-to-alumina ratio of at least 12, a constraint index of about 1 to 12 and acid cracking activity (alpha value) of about 1–250, preferably about 3 to 80 based on total catalyst weight. In the fluidized bed reactor the coked catalyst preferably has an apparent activity (alpha value) of about 1 to 20 under the process conditions to achieve the required degree of reaction severity. Representative of the ZSM-5 type medium pore shape selective zeolites are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, and ZSM-48. Aluminosilicate ZSM-5 is disclosed in U.S. Pat. No. 3,702,886 and U.S. Pat. No. Re. 29,948. Other suitable zeolites are disclosed in U.S. Pat. Nos. 3,709,979; 3,832,449; 4,076,979; 3,832,449; 4,076,842; 4,016,245; 4,414,423; 4,417,086; 4,517,396 and 4,542,251. The disclosures of these patents are incorporated herein by reference. While suitable zeolites having a coordinated metal oxide to silica molar ratio of 12:1 to 200:1 or higher may be used, it is advantageous to employ a standard ZSM-5 having a silica alumina molar ratio of about 25:1 to 70:1, suitably modified if desired to adjust acidity and oligomerization/aromatization characteristics. A typical zeolite catalyst component having Bronsted acid sites may consist essentially of aluminosilicate ZSM-5 zeolite.

Certain of the ZSM-5 type medium pore shape selective catalysts are sometimes known as pentasils. In addition to the preferred aluminosilicates, the gallosilicate, the ferrosilicate materials may be employed. ZSM-5 type pentasil zeolites are particularly useful in the process because of their regenerability, long life and stability under the extreme conditions of operation. Usually the zeolite crystals have a crystal size from about 0.01 to 2 microns or more. In order to obtain the desired particle size for fluidization in the turbulent regime, the zeolite catalyst crystals are bound with a suitable inorganic oxide, such as silica, alumina, etc. to provide a zeolite concentration of about 5 to 95 wt. %. It is advantageous to employ a standard ZSM-5 having a silica:alumina molar ratio of 25:1 or greater in a once-through fluidized bed unit to convert 60 to 100 percent, preferably at least 75 wt %, of the monoalkenes and methanol in a single pass. In the preferred embodiment 25% H-ZSM-5 catalyst calcined with 75% silica-alumina matrix binder is employed unless otherwise stated.

Fluidized Bed Reactor Operation

Suitable olefinic feedstreams to the olefin upgrading unit comprise C_2–C_4 alkenes, including unreacted butylenes and other alkenes from the etherification operation. Non-deleterious components, such as C_4 lower paraffins and inert gases, may be present. The reaction severity conditions can be controlled to optimize yield of olefinic gasoline or C_6–C_8 BTX hydrocarbons, according to product demand. Reaction temperatures and contact time are also significant factors in the reaction severity, and the process parameters are followed to give a substantially steady state condition wherein the reaction severity is maintained within the limits which yield a desired weight ratio of propane to propene in the reaction effluent.

In a turbulent fluidized catalyst bed the conversion reactions are conducted in a vertical reactor column by passing hot reactant vapor or lift gas upwardly through the reaction zone at a velocity greater than dense bed transition velocity and less than transport velocity for the average catalyst particle. A continuous process is operated by withdrawing a portion of coked catalyst from the reaction zone, oxidatively regenerating the withdrawn catalyst and returning regenerated catalyst to the reaction zone at a rate to control catalyst activity and reaction severity to effect feedstock conversion. However, the processes may be operated without employing a catalyst regenerator.

In a typical process, the alkanol and olefinic feedstream is converted in a catalytic reactor under oligomerization conditions and moderate pressure (ie-100 to 2500 kPa) to produce a predominantly liquid product consisting essentially of C_5+ hydrocarbons rich in gasoline-range mono-olefins and aromatics. The C_5+ gasoline product comprises at least 45 weight percent aromatics. The use of fluidized bed catalysis allows excellent control of catalyst activity and temperature which can be used to maintain relatively constant product quality. In addition, it provides excellent flexibility to change operating conditions.

The light aliphatic hydrocarbon conversion process to form aromatics may utilize conversion conditions described in U.S. Pat. Nos. 3,760,024 (Cattanach); 3,845,150 (Yan and Zahner); 4,097,367 (Haag et al.); 4,350,835 (Chester et al.); 4,590,323 (Chu); and 4,629,818 (Burress) incorporated herein by reference. Preferred aromatization conditions include temperatures of about 400° C.-600° C. and pressure from about 100-2000 kpa, absence of hydrogen and a weight hourly space velocity of from 0.5 to 20 WHSV. The C6-C10 aromatic products which are produced are predominantly benzene, toluene and xylene isomers (BTX) with minor amounts of other C_6-C_{10} components.

While the instant invention has been described by specific examples and embodiments, there is no intent to limit the inventive concept except as set forth in the following claims.

What is claimed is:

1. A continuous process for converting lower aliphatic alkanol and olefinic hydrocarbon to alkyl tertiary-alkyl ethers and C_5+ gasoline boiling range hydrocarbons comprising the steps of:

   (a) contacting alkanol and a light olefinic hydrocarbon stream rich in isobutylene and other C_4 isomeric hydrocarbons under iso-olefin etherification conditions in an etherification reaction zone containing acid etherification catalyst;

   (b) separating etherification effluent from step (a) to recover a light stream comprising unreacted alkanol and light olefinic hydrocarbon and a liquid product stream containing alkyl tertiary-butyl ether; and

   (c) contacting said light stream with acidic, medium pore metallosilicate catalyst under alkanol and hydrocarbon conversion conditions whereby C_5+ gasoline boiling range hydrocarbons are produced.

2. The process of claim 1 wherein said alkanol is selected from the group comprised of methanol, ethanol, 1-propanol, isopropanol, 1-butanol, 2-butanol and mixtures thereof.

3. The process of claim 1 wherein the alkanol feedstock comprises dry methanol and wherein the hydrocarbon consists essentially of C_4 paraffins and olefins.

4. The process of claim 1 wherein step (b) alkyl tertiary-butyl ether comprises methyl tertiary butyl ether.

5. The process of claim 1 wherein said light olefinic hydrocarbon stream comprises C_4+ olefinic hydrocarbons and said liquid stream contains alkyl tertiary butyl ether and alkyl tertiary amyl ether.

6. The process of claim 5 wherein said alkanol comprises methanol.

7. The process of claim 1 wherein step (c) alkanol and hydrocarbon conversion conditions comprise temperature between 400° and 600° C., pressure between 100 and 7000 kPa, and said gasoline boiling range hydrocarbons are rich in C_6-C_9 aromatic hydrocarbons.

8. The process of claim 1 wherein step (c) alkanol and hydrocarbon conversion conditions comprise a temperature of about 425° C., pressure of about 925 kPa, and said gasoline boiling range hydrocarbons are predominantly aromatic hydrocarbons.

9. The process of claim 1 wherein said light olefinic hydrocarbon stream consists essentially of C_4 hydrocarbon rich in isobutylene.

10. The process of claim 9 wherein said light hydrocarbon stream comprises about 80 weight percent mixed butanes and butenes.

11. The process of claim 1 wherein said metallosilicate catalyst comprises acid zeolite having the structure of ZSM-5.

12. The process of claim 1 wherein said etherification catalyst comprises acidic zeolite or sulfonated vinyl aromatic resins.

13. An improved process for reacting methanol feedstock with light olefinic hydrocarbons rich in isobutylene to produce C_5+ alkyl tertiary-alkyl ether, which comprises: contacting the methanol feedstock with a hydrocarbon feedstock comprising predominantly isobutylenerich mono-olefins under etherification reaction conditions in contact with an acid etherification catalyst to produce ether product; separating ether product from unreacted methanol and light olefinic hydrocarbons; and converting said unreacted methanol and olefinic hydrocarbons to C_5+ gasoline boiling range hydrocarbons in contact with acidic, medium pore, metallosilicate catalyst.

14. The process of claim 13 wherein said alkyl tertiary alkyl ether comprises methyl tertiary butyl ether.

15. The process of claim 13 wherein said light olefinic hydrocarbon stream consists essentially of C_4 olefins and paraffins.

16. The process of claim 13 wherein said unreacted methanol and olefinic hydrocarbons conversion conditions comprise temperature between 250° and 400° C., pressure between 100 and 2000 kPa, and said gasoline boiling range hydrocarbons are rich in distillate hydrocarbons.

17. The process of claim 16 wherein C_5+ gasoline product comprises at least 45 weight percent aromatics.

18. The process of claim 13 wherein said metallosilicate catalyst comprises acidic, medium pore zeolite.

19. The process of claim 18 wherein said zeolite comprises ZSM-5.

20. The process of claim 13 wherein said etherification catalyst comprises sulfonated vinyl aromatic resins.

21. A continuous process for converting alkanol to alkyl tertiary-alkyl ethers and C_5+ gasoline boiling range hydrocarbons comprising the steps of:

   (a) contacting alkanol and a light olefinic hydrocarbon stream containing C_4+ iso-olefin hydrocarbons under iso-olefins etherification conditions in an etherification reaction zone containing acid etherification catalyst, wherein the molar ratio of said alkanol to iso-olefin is between about 0.7 and 2;

   (b) separating the etherification effluent from step (a) to recover a stream containing unreacted olefinic hydrocarbons and a liquid stream containing alkyl tertiary alkyl ether; and

   (c) contacting said unreacted olefinic hydrocarbon stream with acidic, medium pore metallosilicate catalyst under hydrocarbon conversion conditions whereby C_5+ gasoline boiling range hydrocarbons are produced.

22. The process of claim 21 wherein said alkanol is methanol, ethanol, 1-propanol, isopropanol, 1-butanol, 2-butanol or mixtures thereof.

23. The process of claim 22 wherein the alkanol feedstock comprises dry methanol and wherein the light olefinic hydrocarbon consists essentially of C_4 paraffins

and olefins, and wherein step (b) alkyl tertiary alkyl ether comprises methyl tertiary butyl ether.

24. The process of claim **21** wherein said light olefinic hydrocarbon stream comprises C_4+ olefinic hydrocarbons and said liquid stream contains alkyl tertiary butyl ether and alkyl tertiary amyl ether.

25. The process of claim **21** wherein step (c) hydrocarbon conversion conditions comprise temperature between 250° and 400° C., pressure between 100 and 2000 kPa, and said gasoline boiling range hydrocarbons are rich in distillate hydrocarbons.

26. In the process for converting alkanol to alkyl tertiary-alkyl ethers comprising the steps of:

contacting alkanol and a light olefinic hydrocarbon stream rich in isobutylene and other C_4 isomeric hydrocarbons under iso-olefin etherification conditions in an etherification reaction zone containing acid etherification catalyst; and separating etherification zone effluent to recover a vapor stream comprising unreacted alkanol and light olefinic hydrocarbon and a liquid product stream containing alkyl tertiary-butyl ether; the improvement comprising;

contacting said unreacted alkanol and light olefinic hydrocarbon vapor stream with acidic, medium pore metallosilicate catalyst under alkanol and hydrocarbon conversion conditions whereby aromatic hydrocarbons are produced.

27. The process of claim **26** wherein said alkanol comprises methanol, said hydrocarbon comprises C_4 paraffins and olefins and said alkyl tertiary-butyl ether comprises methyl tertiary butyl ether.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,001,292

DATED : Mar. 19, 1991

INVENTOR(S) : Harandi et al.

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

The Drawing Sheet, consisting of FIG. 1, as shown on the attached page, should be added.

Signed and Sealed this

Twenty-fifth Day of August, 1992

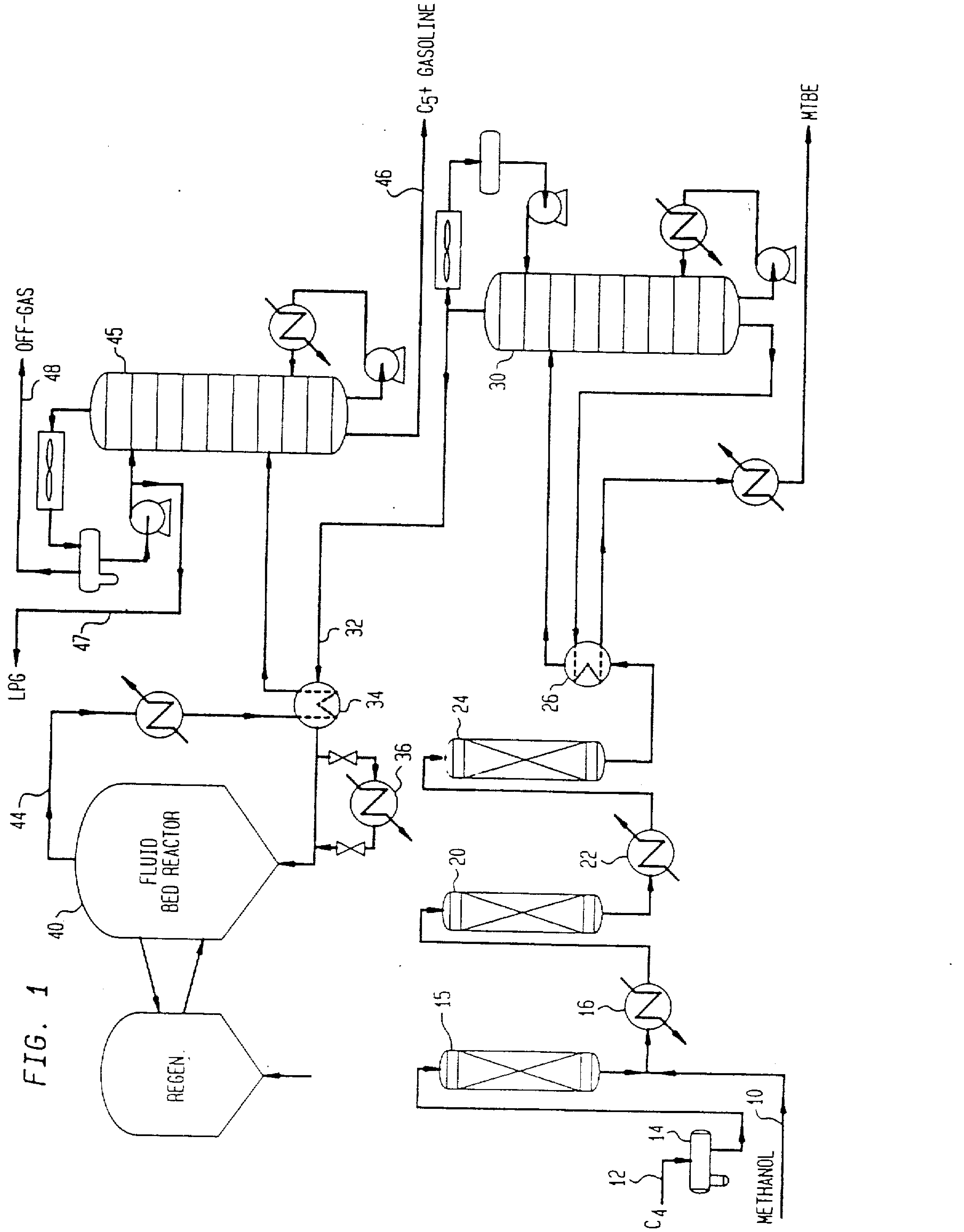
Attest:

DOUGLAS B. COMER

Attesting Officer

Acting Commissioner of Patents and Trademarks

FIG. 1


C$_5$+ GASOLINE
46
MTBE
OFF-GAS
48
45
30
LPG
47
32
34
44
FLUID BED REACTOR
40
36
REGEN.
24
26
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14
12
C$_4$
METHANOL

UNITED STATES PATENT AND TRADEMARK OFFICE

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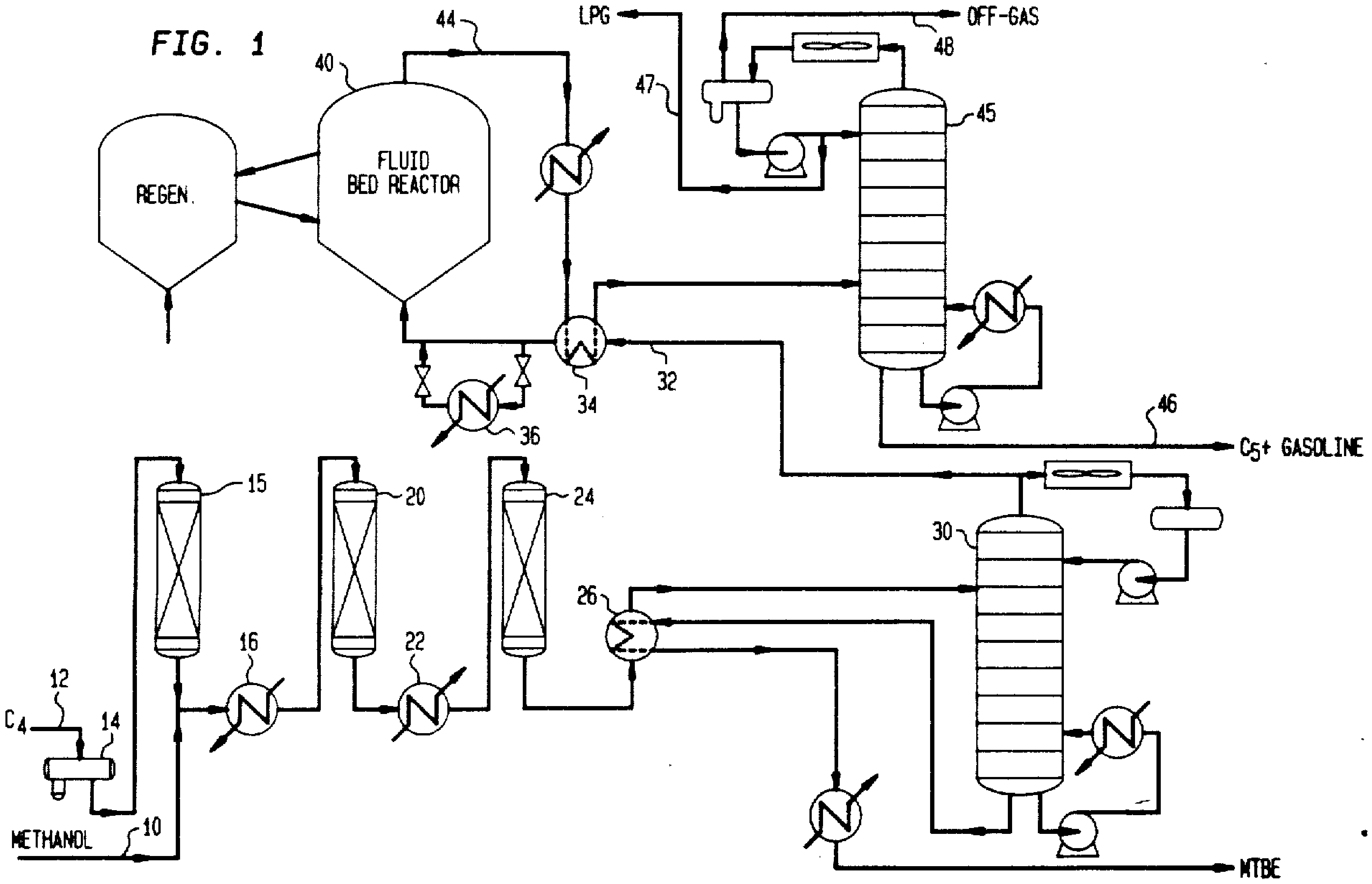
FIG. 1


44
40
FLUID BED REACTOR
REGEN.
LPG
OFF-GAS
48
47
45
34
32
36
46
C_5+ GASOLINE
15
20
24
30
26
16
22
12
C_4
14
METHANOL
10
MTBE